Fuel 95 (2012) 15–18

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Determination of phosphorus in biodiesel using 1:12 phosphomolybdic modified electrode by cyclic voltammetry

Tina Rita Celli Zezza *, Michelle de Souza Castilho, Nelson Ramos Stradiotto

Department of Analytical Chemistry, Institute of Chemistry-Araraquara, São Paulo State University, UNESP, Rua Francisco Degni 55, Bairro Quitandinha, 14800-900 Araraquara, SP, Brazil

ARTICLE INFO

Article history:
Received 19 March 2010
Received in revised form 17 December 2011
Accepted 17 December 2011
Available online 3 January 2012

Keywords:
Biodiesel
Modified electrodes
1:12 Phosphomolybdic
Phosphorus

ABSTRACT

In this work, a 1:12 phosphomolybdic film modified glassy carbon electrode is prepared by electrochemical deposition and its application was studied by cyclic voltammetry. The film modified electrode is used for the determination of phosphorus and exhibits a linear response to phosphorus in the concentration of 7.0×10^{-6}–8.0×10^{-5} mol L^{-1} with a detection limit of 8.7×10^{-6} mol L^{-1}. This method has been used for determination of phosphorus in the form of phosphate in biodiesel samples with satisfactory results.

1. Introduction

The petroleum market instability, the limited availability of crude oil and, mainly, the serious impact of petroleum-based fuels use on the environment have currently stimulated the spread of alternative fuels [1,3]. Many researches have been held on biodiesel, an alternative fuel for diesel engines that has recently obtained increasing attention worldwide [2,4]. This alternative fuel has a number of advantages including: reduction of toxic exhaust emissions – lower amounts of hydrocarbon, carbon monoxide and particulate emissions; greenhouse gas savings – carbon dioxide produced by burning biodiesel is used by subsequent crops that are, then, used to produce the fuel; low sulfur content; fast biodegradability – approximately 4–5 times as fast as petroleum diesel; lower toxicity than petrodiesel; higher flashpoint than petroleum diesel; it can be used in diesel engines with little or no modification. Feedstocks such as soy, canola, mustard, sunflower, coconut, palm and cottonseed oil as well as beef tallow and fish oils have been used to manufacture biodiesel [5].

Among the several processes used for the production of biodiesel, esterification and transesterification are distinguished, in particular the latter, which is used in large scale production. Any chemical reaction, including the transesterification, is rarely completed and usually the products of the reaction, in this case the alkyl esters, are contaminated [6]. The contaminants to be considered include water, free glycerin, bound glycerin, alcohol, free fatty acids, soaps, and residual catalyst. The presence of inorganic contaminants is related to the efficiency of the wash.

The phosphorus found in biodiesel stems from phospholipids (animal and vegetable material) contained in the feedstock and from used frying oil. High levels of phosphorus have been shown to damage catalytic converters used in emission control systems [7]. Since the presence of contaminants can lead to operational problems, the American Society for Testing and Material (ASTM) and European Standard (EN) have developed standards to which pure biodiesel (B100) can be tested. A maximum level of 10 mg kg^{-1} of phosphorus in biodiesel samples has been established. Standard method for determination of phosphorus is an inductively coupled plasma atomic emission spectrometry (ICP-OES), according to ASTM 4951 [8]. Several studies reported in the literature show experiments with satisfactory results for determination of phosphorus in biodiesel using the technique established by ASTM official.

The phosphorus ions have been determined in several matrices using different techniques such as spectrophotometry [9,10], chromatography [11,12] and electrochemistry [13–25].

Among the various methods used for electroanalytical determination of phosphate, we can cite the method developed by Fogg et al. [13] that determined phosphate with β-heteropolymolybdates on a glassy carbon electrode, using the technique of differential pulse voltammetry. The 12-molybdophosphate produces an anodic wave on glassy carbon electrode, which is used as the basis of the method for determination of phosphate.

Osakai et al. [14] developed a sensor using the electrochemical formation of a heteropolyanion at the interface between an

* Corresponding author. Tel.: +55 16 3301 6621; fax: +55 16 3322 7932.
E-mail address: tinacelli@uol.com.br (T.R.C. Zezza).

0016-2361
doi:10.1016/j.fuel.2011.12.035

aqueous solution and sample solution containing the anion of nitrobenzene hexamolybdate, the voltammetric current proportional to the concentration of phosphate in a range of 2.0×10^{-5}–5.0×10^{-4} mol L^{-1}.

A modified carbon paste electrode [15] with a film of 1:12 phosphomolybdate was prepared by electrochemical deposition for the determination of phosphorus in phytic acid with a linear range of concentration from 0.4 a 25 g mL^{-1} and the detection limit of 0.04 g mL^{-1}.

Biosensors have been used for the determination of phosphate; the method proposed by Su and Mascini [16] consists of a platinum electrode modified with a film of polyphenol containing two enzymes, alkaline phosphatase and glucose oxidase. The method was efficient for the determination of phosphate, with a detection limit of 4.0×10^{-6} mol L^{-1}.

The phosphate ions can also be determined using the ion selective electrodes [17–25]. Among these, a method [17] stands out, using an ion selective glass electrode, which is the detection limit of 2.2×10^{-7} g mL^{-1} with a coefficient of variation of 0.3%.

Finally, De Marco and Phan [18] used a cobalt wire electrode for potentiometric determination of phosphate in hydroponic nutrient solutions in the linear concentration of 5.0×10^{-4}–1.0×10^{-2} mol L^{-1}.

In view of the importance of biodiesel as an alternative fuel and considering that the presence of inorganic contaminants, such as phosphorus, which causes damage to catalytic conversion and causes an increase in particulate emission, besides the fact that the official methods of analysis involving equipment is very costly, the goal is to develop an alternative methodology using electrodes chemically modified with 1:12 phosphomolybdic for determination of phosphorus in biodiesel.

2. Experimental

2.1. Reagents and apparatus

All chemicals were of analytical grade and the solutions were prepared using deionized water from Milli-Q (Millipore, USA). KH_2PO_4 (Merck), H_2SO_4 (Merck), $(NH_4)_6Mo_7O_{24}.4H_2O$ (Merck), acetone (Merck) were used without further purification.

Electrochemical experiments were performed on potentiostat from Auto-Lab, Model PGSTAT 30, which was used for cyclic voltammetric measurements. The electrolytic cell with a 10 mL volume and three electrodes systems were used: a glassy carbon disk, $A = 0.07$ cm^2, used as the working electrode, a platinum wire as an auxiliary electrode and $Ag/AgCl_{sat}$ as the reference electrode. The glassy carbon electrode was polished to a mirror finish with alumina (0.5 μm) and then rinsed thoroughly with water. Dry nitrogen was passed through the solution to remove oxygen and was kept flowing over the solution during runs.

2.2. Electrode modification

1:12 Phosphomolybdic (PMo_{12}) film was prepared by voltammetric cycling of the glassy carbon electrode in a solution of 3.0×10^{-3} mol L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$; 0.5 mol L^{-1} H_2SO_4; 16% V/V acetone and 1.0×10^{-4} mol L^{-1} KH_2PO_4 in an oxygen free solution. For the film formation, 10 successive potential cycles from 0.6 to 0.1 V (vs. $Ag/AgCl_{sat}$) were carried out using a scan rate of 100 mV s^{-1}.

2.3. Analytical procedure

The electrode was voltammetrically cycled and characterized in a solution of 3.0×10^{-3} mol L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$; 0.5 mol L^{-1} H_2SO_4; 16% V/V acetone and 1.0×10^{-4} mol L^{-1} KH_2PO_4 in an oxygen free solution. The electrode was cycled between 0.6 and 0.1 V (vs. $Ag/AgCl_{sat}$) at 100 mV s^{-1} for ten successive cycles. After each determination, the 1:12 phosphomolybdic electrode needed rinsing water. All measurements were performed in triplicate.

The biodiesel samples of soy oil analyzed were obtained from Paraná Technological Institute (TECPAR) in Brazil. Among the methods for extraction of phosphorus in biodiesel in the literature, it is common to use a solvent extractor or water. This allows the formation of two phases, one organic and one aqueous, and the phosphorus is miscible in the aqueous phase.

Firstly, a liquid–liquid extraction was done using H_2SO_4 1.0 mol L^{-1}. The phosphorus present in biodiesel is produced from phospholipids in the presence of acids, releasing the phosphorus in the form of phosphate, which was determined using the method developed.

3. Results and discussion

3.1. 1:12 Phosphomolybdic modified electrode

The cyclic voltammogram of the film formation of 1:12 phosphomolybdic at glassy carbon with a scan rate of 100 mV s^{-1} in a potential range of 0.6–0.1 V, after 10 successive scans is shown in Fig. 1. In the cyclic voltammogram, two pairs of well-defined oxidation – redox pair waves were obtained: at 0.21/0.17 V and at 0.38/0.33 V.

The modification solution was acidified with sulfuric acid, because of the solution of molybdate in acid medium, the phosphate is converted into anions ($PMo_{12}O_{40}^{3-}$) showed in Eq. (1) [26]; more than half in the neutral or basic solution undergoes hydrolysis processes [27] and the pH 10 film is destroyed with the disappearance of the peaks [28].

Acetone can be used as a stabilized reagent in analysis. For a modification without acetone, the peak height increased with the time and with the addition of 16% (V/V) acetone the peak height increased and became stable and the β- phosphomolybdic is not converted in α-phosphomolybdic.

$$7PO_4^{-3} + 12Mo_7O_{24}^{6-} + 72H^+ \rightarrow 7PMo_{12}O_{40}^{3-} + 36H_2O \quad (1)$$

In a solution containing 1.0×10^{-4} mol L^{-1} of phosphorus, the relation $\frac{ip_a}{ip_c}$ of two peaks is approximately 1,0 indicating that the process is reversible. The possible stoichiometry is:

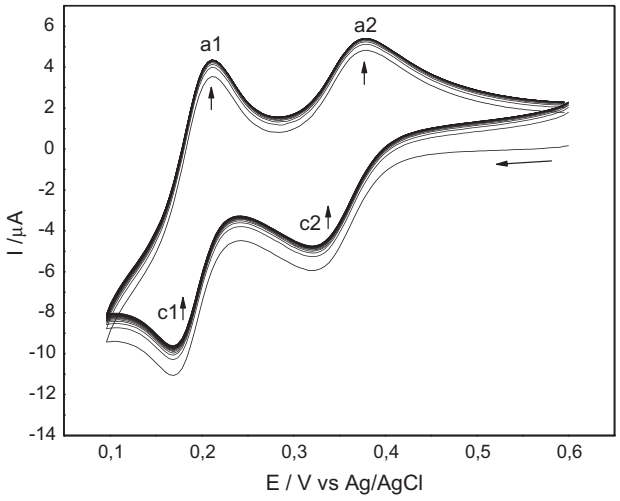

Fig. 1. Cyclic voltammograms of a solution containing 3.0×10^{-3} mol L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 0,5 mol L^{-1} H_2SO_4, 16% (V/V) de acetone and 1.0×10^{-4} mol L^{-1} KH_2PO_4 (= 100 mV s^{-1}).

$$[PMo_{12}O_{40}]^{3-} + 2e^- + 2H^+ \rightleftharpoons [H_2PMo_2^{V}Mo_{10}^{VI}O_{40}]^{3-} \quad (2)$$

$$[H_2PMo_2^{V}Mo_{10}^{VI}O_{40}]^{3-} + 2e^- + 2H^+ \rightleftharpoons [H_4PMo_4^{V}Mo_8^{VI}O_{40}]^{3-} \quad (3)$$

The effect of scan rate on the peak currents were examined over rang 20–200 mV s^{-1} in a solution containing 1.0×10^{-4} mol L^{-1} of phosphorus. According to the equations $Ip_{c1} = -0.025 + 0.32\ v^{1/2}$; $Ip_{c2} = -0.79 + 0.49\ v^{1/2}$; $Ip_{a1} = 0.20 + 0.32\ v^{1/2}$; $Ip_{a2} = 0.10 + 0.55\ v^{1/2}$ and their correlation coefficients 0.9999; 0.9994; 0.9995; 0.9988, it showed that the peak currents increased linearly with the square root of scan rate, as expected for a diffusion-controlled.

3.2. Development of analytical methodology

In order to check the influence of phosphorus at the 1:12 phosphomolybdic, modified electrode aliquots with different concentration of phosphorus were added to the electrochemical cell (Fig. 2). All the four peaks had linear relationships between the peak currents and the phosphorus concentration over the range 7.0×10^{-6}–8.0×10^{-5} mol L^{-1}. The linear regression equations and the correlation coefficients were as follows:

$$Ip_{c1} = 0.66 + 3.76 \times 10^4 c \qquad r = 0.9906 \quad (4)$$

$$Ip_{c2} = 1.25 + 6.31 \times 10^4 c \qquad r = 0.9974 \quad (5)$$

$$Ip_{a1} = 0.35 + 4.55 \times 10^4 c \qquad r = 0.9934 \quad (6)$$

$$Ip_{a2} = 1.44 + 6.71 \times 10^4 c \qquad r = 0.9939 \quad (7)$$

From these, it can be seen that Ip_{c2} and Ip_{a2} had better results taking into account the values of correlation coefficients. The Ip_{c2} showed a better correlation coefficient, a lower detection limit 8.7×10^{-6} mol L^{-1} (calculated by the IUPAC method) and a sensitivity of 6.31×10^4 μA/μmol L^{-1}.

In order to evaluate the selectivity of the method, ions like sodium, potassium, calcium and magnesium were added to the electrochemical cell, because, according to the specifications of ASTM and EN [8], these ions are inorganic contaminants present in biodiesel. However, no significant changes have happened in peak currents.

According to Calvo et al. [28], the major problem, in the determination of phosphorus in 1:12 phosphomolybdic modified electrode, would be the presence of silicate, because when present in this sample, it can form complexes similar to that of phosphorus with molybdate. However, this ion is not a problem in the determination of phosphorus into biodiesel, because biodiesel is substantially free of silicate.

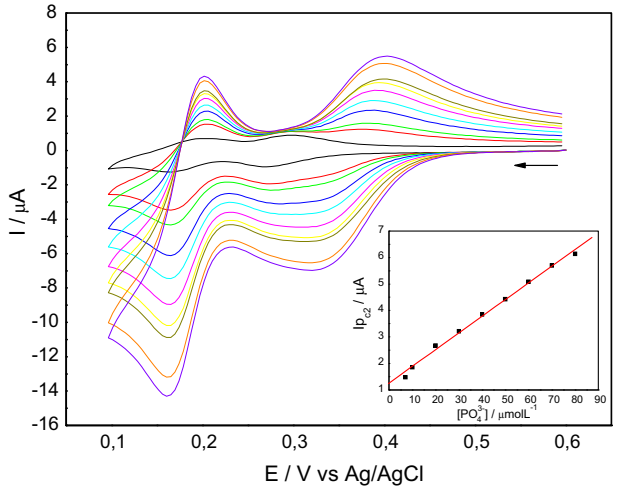

Fig. 2. Influence of phosphorus concentration in the electrode chemically modified with 1:12 phosphomolybdic in a solution containing 3.0×10^{-3} mol L^{-1} $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 0.5 mol L^{-1} H_2SO_4 and 16% (V/V) acetone.

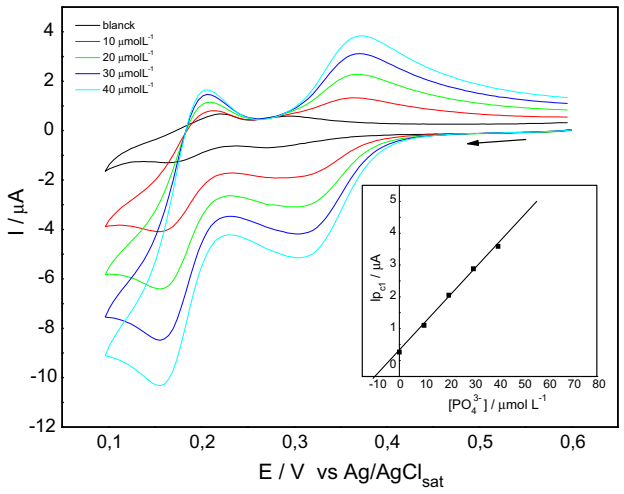

Fig. 3. Cyclic voltammograms of standard addition in a solution containing 3.0×10^{-3} mol L^{-1} ammonium molybdate, biodiesel extracted with 1.0 mol L^{-1} sulfuric acid and 16% (V/V) acetone.

Table 1
Determination of phosphorus in biodiesel sample and recovery methods.

$[PO_4^{3-}]$/μmol L^{-1} - added	$[PO_4^{3-}]$/μmol L^{-1} - found	Recovery (%)
10.0	9.63 ± 0.11	96.00
20.0	20.9 ± 0.09	105.00
30.0	30.7 ± 0.24	102.00
40.0	39.1 ± 0.07	98.00

3.3. Determination of phosphorus in biodiesel sample

After the liquid-liquid extraction with H_2SO_4 1.0 mol L^{-1} and analyzing the results obtained (Fig. 3) it was possible to verify the phosphorus concentration in the biodiesel sample. Through the method of standard addition, it was obtained 1.36 ± 0.14 mg kg^{-1} of phosphorus in the sample of biodiesel, lower than permitted by ASTM and European Biodiesel Standards (10 mg kg^{-1}).

In order to evaluate the validity of the proposed method, recovery studies were carried out on samples to which known amounts of phosphorus had been added. (Table 1).

4. Conclusion

Simple and selective procedures for determination of phosphorus using cyclic voltammetry were established with 1:12 phosphomolybdic modified electrode. The reported method has been successfully tested for the determination of phosphorus in biodiesel sample. A linear relationship in the range (7.0×10^{-6}–8.0×10^{-5} mol L^{-1}) is obtained. The detection limit of phosphorus is 8.7×10^{-6} mol L^{-1}. The data obtained with the recovery indicates the reliability of the method.

Acknowledgements

The authors gratefully acknowledge the financial support from CAPES, CNPq and Paraná Technological Institute (TECPAR).

References

[1] Monteiro MR, Ambrozin ARP, Lião LM, Ferreira AG. Critical review on analytical methods for biodiesel characterization. Talanta 2008;77:593–605.
[2] Filho LCG, Micke GA. Development and validation of a fast method for determination of free glycerol in biodiesel by capillary electrophoresis. J Chromatogr A 2007;1154:477–80.
[3] Santos EJ, Herrmann AB, Chaves ES, Vechiatto WWD, Shoemberger AC, Frescura VLA, et al. Simultaneous determination of Ca, P, Mg, K and Na in biodiesel by axial view inductively coupled plasma optical emission spectrometry with internal standardization after multivariate optimization. J Anal At Spectrom 2007;22:1300–3.
[4] Gerpen JV. Biodiesel processing and production. Fuel Process Technol 2005;86:1097–107.
[5] Dantas MB, Almeida AAF, Conceição MM, Fernandes VJJ, Santos IMG, Silva FC, et al. Characterization and kinetic compensation effect of corn biodiesel. J Therm Anal Calorim 2007;87:847–51.
[6] Castilho MS, Stradiotto NR. Determination of potassium ions in biodiesel using a nickel(II) hexacyanoferrate-modified electrode. Talanta 2008;74:1630–4.
[7] Bowman M, Hilligoss D, Rasmussen S, Thomas R. Biodiesel: a renewable and biodegradable fuel. Hydrocarbon Process 2006;85:103–6.
[8] <http://www.anp.gov.br>. [30.11.09].
[9] Nagai M, Sugiyama M, Hori T. Sensitive spectrophotometric determination of phosphate using silica – gel collectors. Anal Sci 2004;20:341–4.
[10] El–Sayed AAY, Hussein YZ, Mohammed MA. Simultaneous determination of phosphate and silicate by first – derivative spectrophotometry. Anal Sci 2001;17:1461–4.
[11] De Medina HL, Gutierrez E, González G, Marin J, Andueza E. Determination of phosphate and sulphide in natural waters in the presence of high sulphate concentrations by chromatography under isocratic conditions. J Chromatogr A 1996;739:207–15.
[12] Henin O, Barbier B, Brack A. Determination of phosphate and pyrophosphate ions by capillary electrophoresis. Anal Biochem 1999;270:181–4.
[13] Fogg AG, Bsebsu NK, Birch BJ. Differencial pulse anodic voltammetric determination of phosphate, silicate, arsenate and germanate as beta – heteropolymolybdates at a stationary glass carbon electrode. Talanta 1981;28:473–6.
[14] Osakai T, Himeno S, Saito A, Katano H. A voltammetric phosphate sensor based on heteropolyanion formation at the nitrobenzene water interface. Electroanalysis 1993;5:215–9.
[15] Guanghan L, Xiaogang W, Yanhua L, Shenlai Y. Studies on 1:12 phosphomolybdic heteropoly anion film modified carbon paste electrode. Talanta 1999;49:511–5.
[16] Su YS, Mascini M. AP – GOD biosensor based on a modified poly (phenol) film electrode and its application in the determination of low levels of phosphate. Anal Lett 1995;28:1359–78.
[17] Derkasova VG, Kareli NVA, Moskalenko LA, Potapova TM. Potentiometric determination of phosphate ions with a glass electrode. Zh Anal Khim 1989;14:873–6.
[18] De Marco R, Phan C. Determination of phosphate in hydroponic nutrient solutions using flow injection potentiometry and a cobalt wire phosphate ion selective electrode. Talanta 2003;60:1215–21.
[19] Chen ZL, Grierson P, Adams MA. Direct determination of phosphate in soil. Direct determination of phosphate in soil extracts by potentiometric flow injection using a cobalt wire electrode. Anal Chim Acta 1998;363:191–7.
[20] Nikiforova TG, Russkikh YaV. Use of voltammetry for determination of phosphate and sulfate anions in aqueous media. Zh Anal Khim 1995;50:315–8.
[21] Conrath N, Gruendig B, Huewel S, Cammann K. A novel enzyme sensor for the determination of inorganic phosphate. Anal Chim Acta 1995;309:47–52.
[22] Kwan RCH, Leung HF, Hon PYT, Barford JP, Renneberg GR. A screen – printed biosensor using pyruvate oxidase for rapid determination of phosphate in synthetic wastewater. Appl Microbiol Biotechnol 2005;66:377–83.
[23] Ikebukuro K, Nishida R, Yamamoto H, Arikawa Y, Nakamura H, Suzuki M, et al. A novel biosensor system for the determination of phosphate. J Biotechnol 1996;48:67–72.
[24] Cox JA, Cheng KH. Determination of phosphate by cathodic stripping voltammetry at a glassy carbon electrode. Anal Lett 1974;7:659–70.
[25] Cosnier S, Gondran C, Watelet JC, De Giovani W, Furriel RPM, Leone FA. An bienzyme electrode (alkaline phosphatase polyphenol oxidase) for the amperometric determination of phosphate. Anal Chem 1998;70:3952–6.
[26] Sun C, Zhao J, Xu H, Sun Y, Zhang X, Shen J. Fabrication of multilayer films containing 1:12 phosphomolybdic anions on the surface of a gold electrode based on electrostatic interaction and its application as an electrochemical detector in flow – injection amperometric detection of hydrogen peroxide. J Electroanal Chem 1997;435:63–8.
[27] Dong S, Jin Z. 1:12 Phosphomolybdic anion modified glassy carbon electrode. J Soc Chem Commun 1987;24:1871–2.
[28] Calvo JQ, Idrissi L, Palleschi G. Investigation of amperometric detection of phosphate application in seawater and cyanobacterial biofilm samples. Talanta 2004;63:567–74.